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Relationships between Direction of Wind Flow and Fine Particle Sulfur Concentrations within and Upwind of St. Louis, MO. (Journal Version)

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16. ABSTRACT

The relationships between the monthly averages of diurnal fine particle sulfur concentrations and wind flow direction with season of the year are evaluated using measurements at urban and rural locations within the St. Louis area. The results confirm and quantify the regional contribution to fine particle sulfur concentrations within the St. Louis urban area. The contribution of local scale photochemical oxidation of SO_2 to particle sulfur is estimated as is the contribution of local scale direct emissions of particle sulfur. Evidence is provided of downward mixing during the morning hours of fine particle sulfur along with O_3 from layers aloft. A positive gradient in fine particle sulfur concentrations from west to east is confirmed which is shown to be primarily the result of much lower concentration in flow from the northwest of the St. Louis area. These results are consistent with other monitoring measurements available from midcontinental non-urban locations.

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RELATIONSHIPS BETWEEN DIRECTION OF WIND FLOW AND FINE PARTICLE SULFUR CONCENTRATIONS WITHIN AND UPWIND OF ST LOUIS, MO

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Abstract—The relationships are considered between monthly and quarterly means of the fine particle sulfur (S) concentrations and wind flow direction, period of day and season of the year. The measurements used are those obtained at selected urban and at rural monitoring stations in the St Louis area during the Regional Air Pollution Study in 1975, 1976 and 1977. Higher mean fine particle S concentrations are observed with wind flows from the E compared to the W and from the NE and SE quadrants compared to the NW quadrant. Substantially higher fine particle S concentrations are obtained with wind flows from the E compared to the W even when conditions are selected so that the values of temperature, solar radiation intensity and wind speed are within the same restricted ranges. A consistent increase in the fine particle S concentrations occurs through the late morning and afternoon with decrease in the evening and especially in the early morning during spring and summer months with wind flows from the E.

The contributions are estimated for local scale and regional scale processes to the observed fine particle S concentrations. Local scale processes include those involving atmospheric formation and primary emissions each contribute 0.6–1.0 and 0.6 $\mu g\ m^{-3}$ of the fine particle S. Regional scale processes account for the greater part of the observed concentrations especially when the wind flows are from the SE or SW. Regional scale episodes involving passage of warm high pressure systems to the E of St Louis with accumulation of precursors made especially significant contributions to formation of fine particle S.

The atmospheric gas phase and liquid phase chemical reactions contributing to the formation of fine particle S are discussed. Emphasis is placed on the effects of chemistry on the seasonal variations in concentrations of fine particle S.

Key word index: Fine particle S, photochemical, wind direction, diurnal variations, local scale, regional scale, anthropogenic precursor emissions.

INTRODUCTION

Several discussions of the aerosol composition measurements obtained at monitoring stations (RAMS) in and around St Louis, MO during the regional Air Pollution Study (RAPS) are available (Alpert and Hopke, 1981; Altshuller 1982, 1984, 1985; Dzubay, 1980; Loo *et al.*, 1978; Trijonis *et al.*, 1980). However, the relationships of fine particle S (S_f) concentrations to direction of wind flow into the St Louis area have received little attention. An improved understanding of the effects of wind flow on the distribution of S_f should be useful in evaluating the regional and urban scale contributions of S_f to particulate mass, acid deposition and to visibility effects.

In the present study the monthly and quarterly means of S_f concentrations obtained from measurements at two monitoring stations within urban/industrial areas, stations 103 and 105, were used along with those at the outer and intermediate ring monitoring stations 118, 120, 122 and 124 when in the inflow of air from upwind into the St Louis area. Measurements of S_f at stations 103 and 105 are of especial interest because 6-h average samples were routinely obtained at these two locations.

The effects of W compared to E wind flows have been shown to be of particular significance in relation to O_3 concentrations (Altshuller, 1986). In the present investigation this aspect is also emphasized as well as wind directional effects on diurnal S_f concentrations within St Louis. The contributions associated with the various processes for S_f formation are estimated for the St Louis area.

PROCEDURE

The measurements of the concentrations of fine particle S, S_f, available from samples of particulate matter in the less than 2.4 μm size fraction collected on dichotomous samplers are utilized as in previous studies (Altshuller, 1982, 1984, 1985). Measurements at two RAMS stations, 103 and 105, after averaging were used as resonable representatives of the core urban and industrial areas in St Louis (Table 1). At these two stations 6-h samples were routinely collected for the periods 0000–0600 h, 0600–1200 h, 1200–1800 h and 1800–2400 h. Complete months of sampling and measurement of S_f, $S_f(U)$, are available at these two stations from July 1975 to March 1977. Measurements at four RAMS sites, stations 118, 120, 122 and 124 were used to obtain regional inflows of S_f, $S_f(R)$, from upwind (Table 1). At sites 118, 120 and 122 24-h average samples are available from July 1975 to either January or February 1977. At station 124 sampling

Table 1. Brief descriptions of sampling locations [see p. 266 of Altshuller (1985) for a detailed map of these site locations]

Station	Location/local environment
103	National City, IL, 8 km NE of station 103/amidst heavy industries, railroad, army depot and vehicular traffic, in open area 0.5 km around site. Power plant 2.2 km to the NW.
105	Within S St Louis/among trucking and warehousing operations. Close to chemical plants. Heavy industry 3 km to E.
118	16 km S of St Louis/on farmland. Petrochemical plant 7 km to the NE.
120	24.5 km W of St Louis within light industrial park with heavy vehicular traffic nearby.
122	45 km N of St Louis/agricultural area with no major pollution source nearby.
124	38.5 km S of St Louis/agricultural area with no major pollution source nearby

ended in August 1976. The measurements at station 120 on the W edge of St Louis are used only when the average daily wind direction was between 225° and 315°. Maps showing the locations of the RAMS stations during the RAPS program in St Louis are readily available in previous publications (Altshuller, 1985; Shreffler and Evans, 1982).

The values of S_f concentrations obtained from 6-h and 24-h samples were stratified each month-by wind quadrant and monthly mean concentrations calculated from these values. The wind flow quadrants selected are from 0.0 to 89.9°, 90.0 to 179.9°, 180.0 to 269.9° and 270.0 to 359.9°. A compilation of daily average 0700–1359 h CST vector average wind directions already available was used to carry out these stratifications (Shreffler and Evans, 1982). The average wind vector each day is an indication of the net drift of the mesoscale air mass during the daytime.

These daytime vector average wind directions might not be adequate for use with 24-h average concentrations. A series of scatter plots have been constructed relating the monthly mean $S_f(U)$ concentrations of the samples with the diurnal sampling times given above to each other as well as with stratification by E, 0.0–179.9°, and by W, 180.0–359.9°, wind flow directions. The correlations obtained are usually high and the slopes very near to 1 for most sets. The results overall indicate that it is acceptable to use 0700–1359 h average meteorological values in evaluations of the 24-h average S_f concentrations.

To evaluate whether a station was in regional inflow air missing high emission areas the weighted ranges about the vector average daily wind flow directors are assumed to equal at least 90° and usually about 120° (Karl, 1978). If the arc missed the St Louis area the station is assumed to be within the regional inflow of air. This requirement was relaxed somewhat in order to use the measurements from station 120.

Evaluations were made of the statistical significances in the differences of the monthly and quarterly mean concentrations of S_f with season, wind flow direction and time of day. Various statistical tests including analysis of variance and Wilcoxon 2-sample test were utilized.

Several power plants and other large industrial sources are located outside of but near St Louis especially to the S of the city. There is the possibility from time to time that a rural site might be fumigated by such a local source. In such a situation the measured value of S_f would not be representative of the regional inflow of air. One indication of a possible fumigation would be concentrations of $S_f(R)$ at a rural site presumably in inflow air which exceeds the concurrent concentrations of $S_f(U)$. On 12 days during the study the $S_f(R)$ concentration at a rural site within inflow air was questionably high and these values were excluded from the subsequent calculations. On 11 of the 12 days these values occurred at site 122 and on the 12th day at site 118. However fumigations by nearby sources are more likely at site 118 than at site 122. Furthermore the wind direction for flow to site 122 on 7 of the 11 days was from the NW. Fumigations by local sources should not be a problem at site 122 with wind flow from the NW. Therefore it appears that many of these questionable values are more likely to be associated with a sampling or analysis problem on these days than with fumigation by a local source. It is considered that such fumigations at worst occur very infrequently and are not likely to affect the results of this study.

RESULTS

Seasonal profiles of fine particle sulfur concentrations at urban locations and in inflow air into St Louis area

The baseline seasonal profiles without stratification for wind direction of the monthly means of the daily 24-h S_f average concentrations, $S_f(U)$, at stations 103 and 105 and at the monitoring stations within inflow air, $S_f(R)$, are shown in Fig. 1. The seasonal profiles of the two curves are very similar throughout the time period of the study. Large decreases in $S_f(U)$ and $S_f(R)$ concentrations occur consistently from summer to winter months. The monthly average $S_f(U)$ and $S_f(R)$ concentrations remain at low concentration levels throughout the cooler months of the year.

The percentages the monthly means of $S_f(R)$ concentrations within the inflow air at outer or intermediate ring stations constitute of the means of $S_f(U)$ concentrations based on concurrent daily measurements average 77% and range monthly from 68 to 87%. No discernible seasonal effect is apparent.

Monthly average concentrations of fine particle sulfur at urban stations: effects of various diurnal averaging times and of the direction of wind flow

The effects of season and wind direction on diurnal $S_f(U)$ concentrations are shown in Figs 2 and 3. In Fig. 2 the monthly mean $S_f(U)$ concentrations are shown for March, May, July, September and October, 1976. Values are given for the diurnal mean values between 0000–0600 h, 0600–1200 h, 1200–1800 h and 1800–2400 h stratified by E and W wind flows. In Fig. 3 the difference values in the monthly mean $S_f(U)$ concentrations $\Delta[(1200\text{–}1800)\text{h} - (0600\text{–}1200)\text{h}]$ and $\Delta[(0600\text{–}1200)\text{h} - (0000\text{–}0600)\text{h}]$ are plotted for E and W wind flows from July 1975 to December 1976.

As shown in Fig. 2, the monthly mean $S_f(U)$ concentrations with E wind flow consistently exceed those with W wind flows for each of the diurnal average times. The differences in mean $S_f(U)$ concentrations for E compared to W flows are statistically significant with $P \leq 0.1$ for the 1200–1800 h and the 1800–2400 h intervals in the months of May, July and September 1976.

The results given in Figs 2 and 3 indicate that with E wind flows the monthly means of $S_f(U)$ concentrations measured during the 1200–1800 h period and the

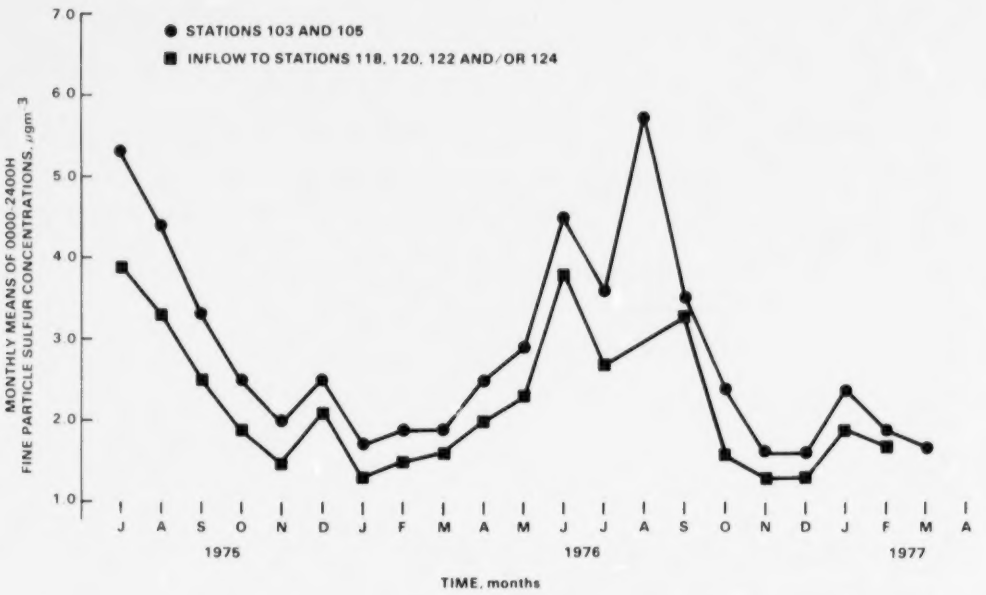

Fig. 1. Monthly averages of the diurnal 24 h average fine particle S concentrations at RAMS stations 103 and 105 and at rural stations within inflow air into the St Louis area during July 1975–March 1977.

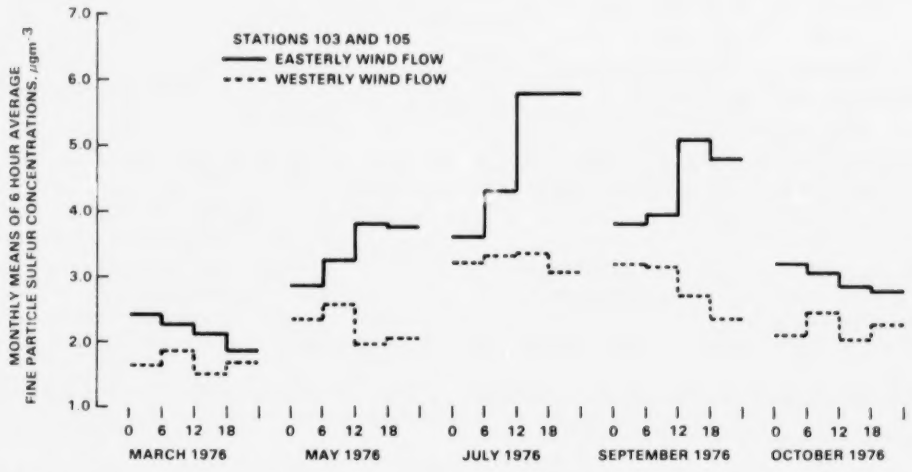

Fig. 2. Monthly averages of the fine particle S concentrations measured during 0000–0600, 0600–1200, 1200–1800 and 1800–2400 h periods at RAMS stations 103 and 105 associated with E and W wind flows for the months of March, May, July, September and October 1976.

1800–2400 h period exceed those measured during the 0000–0600 h and 0600–1200 h periods for the warmer months of 1975 and 1976. Conversely during the cooler months results in Figs 2 and 3 indicate that the monthly means of $S_f(U)$ concentrations during the a.m. periods can exceed those measured during the p.m. periods. With E wind flows the monthly means $S_f(U)$ concentrations tend to be somewhat higher during the 0600–1200 h period than during the 0000–0600 h period especially for the warmer months.

The results given in Figs 2 and 3 indicate with W wind flows that the monthly means of the $S_f(U)$ concentrations during the a.m. periods frequently can equal or exceed those measured during the p.m. periods. With W wind flows the monthly means of the $S_f(U)$ concentrations measured during the 0600–1200 h period usually tend to be somewhat higher than during the 0000–0600 h period. There is no consistent tendency of the diurnal patterns to differ with season for W wind flows (Fig. 2).

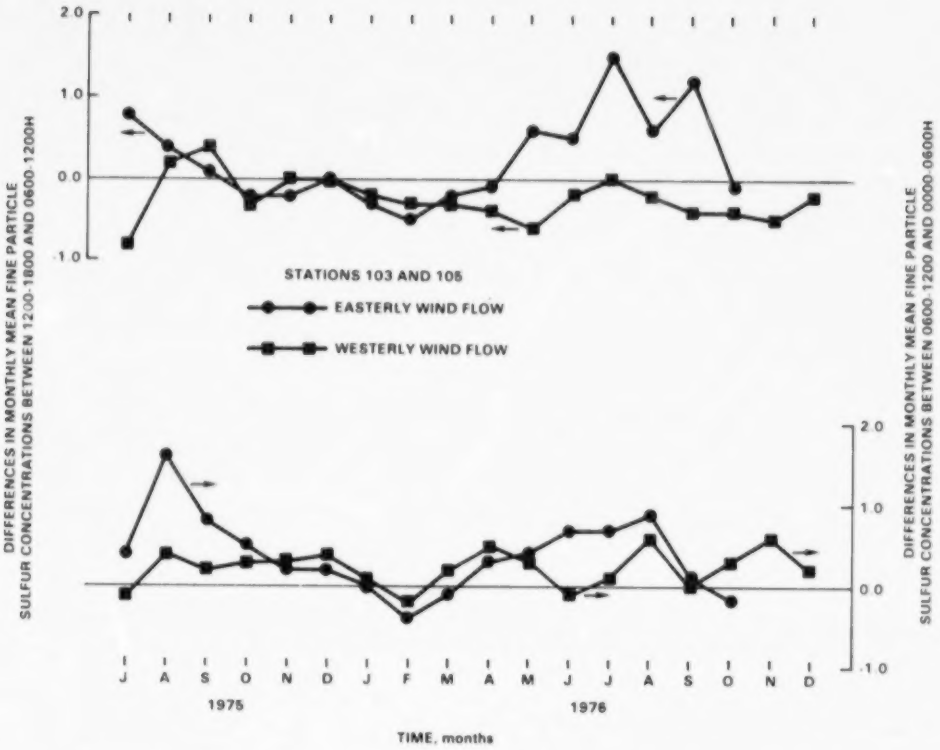
DIFFERENCES IN MONTHLY MEAN FINE PARTICLE SULFUR CONCENTRATIONS BETWEEN 1200-1800 AND 0600-1200H
DIFFERENCES IN MONTHLY MEAN FINE PARTICLE SULFUR CONCENTRATIONS BETWEEN 0600-1200 AND 0000-0600H
2.0
1.0
0.0
-1.0
STATIONS 103 AND 105
EASTERLY WIND FLOW
WESTERLY WIND FLOW
J A S O N D J F M A M J J A S O N D
1975
1976
TIME, months

Fig. 3. Differences in the monthly averages of the fine particle S concentrations between (1) 1200–1800 h and 0600–1200 h periods and (2) 0600–1200 h and 0000–0600 h periods at RAMS stations 103 and 105 associated with E and W wind flows during July 1975–December 1976.

Quarterly means of fine particle sulfur concentrations at urban and rural locations as related to direction of inflow of air masses from downwind

The quarterly mean $S_i(U)$ concentrations associated with flow of air masses into St Louis from the NW are consistently lower than when the wind flows are from either the NE or SE (Table 2). These differences in means are statistically significant with $P \leqslant 0.05$ for NE compared to NW wind flows and with $P \leqslant 0.01$ for SE compared to NW wind flows. Similarly the quarterly mean $S_i(U)$ concentrations associated with wind flows from the E are consistently higher than from the W. Except for the second quarter of 1976 the differences in the quarterly means are statistically significant with $P \leqslant 0.03$ for wind flows from the E compared to the W.

Table 2. Quarterly mean concentrations, standard error of means and number of daily values for particle S concentrations at stations 103 and 105 by wind flow direction into St Louis area

Quarter	Year	Fine particle S concentration ($\mu g\,m^{-3}$) NE	SE	E	SW	NW	W
3rd*	1975	5.27,0.78,14†	5.19,0.70,21†	5.22,0.51‡	4.38,0.38,28	3.17,0.65,25	3.81,0.37
4th	1975	2.98,0.40,11†	2.50,0.20,31†	2.63,0.18‡	2.44,0.19,28	1.39,0.17,19	2.01,0.15
1st	1976	3.00,0.31,7†	2.21,0.20,24†	2.39,0.18‡	1.65,0.12,26	1.43,0.10,34	1.53,0.079
2nd	1976	3.30,0.49,18†	3.39,0.40,25†	3.35,0.31	3.47,0.48,32	2.26,0.60,16	3.07,0.38
3rd*	1976	3.67,0.32,21†	6.30,0.77,18†	4.88,0.44‡	4.22,0.39,29	2.80,0.43,19	3.66,0.31
4th	1976	2.82,0.36,7†	3.14,0.74,7†	2.98,0.40‡	2.05,0.17,31	1.41,0.14,35	1.71,0.12
1st	1977	2.07,NA,1	2.49,0.19,25†	2.47,0.19‡	1.84,0.25,22	1.78,0.16,40	1.80,0.13

* The larger mean particle S concentrations for each quadrant during the third quarter compared to the same quadrants during the first and fourth quadrants the same year are statistically significant (Wilcoxon 2-sample test), P at least 0.05 and usually $P \leqslant 0.01$, except for NE quadrants in 1976.

† The larger mean particle S concentrations with wind flows from the NE or SE compared to those from the NW are statistically significant (Wilcoxon 2-sample test), $P \leqslant 0.05$ (NE) or $P \leqslant 0.01$ (SE).

‡ The larger mean particle S concentrations with wind flows from the E compared to the W are statistically significant, $P \leqslant 0.03$.

The lack of statistical significance in the results for the second quarter are associated with a slightly higher monthly mean $S_f(U)$ concentration when the wind flow is from the W during April 1976.

The quarterly mean $S_f(R)$ concentrations associated with flows of air into the St Louis area from the NW are almost always lower than when the wind flows are from either the NE or SE (Table 3). The differences in means are statistically significant with $P \leq 0.003$ for SE compared to NW wind flows. The quarterly mean $S_f(R)$ concentrations associated with wind flows from the E are consistently higher than with wind flows from the W. Excepting the second quarter of 1976, the differences in the means are statistically significant with $P \leq 0.06$ for wind flows from the E compared to the W.

DISCUSSION

In the discussion to follow both the chemical and meteorological processes which may contribute to the observed patterns in S_f concentrations in the St Louis area are considered. Wind directional effects upon the diurnal and seasonal patterns of S_f will be discussed.

The diurnal patterns in the S_f concentrations at sites 103 and 105 during the third quarters of 1975 and 1976 when the air flows are from the NE or SE will be emphasized in the first part of this discussion. The S_f concentrations increase from the 0000–0600 h interval to the 0600–1200 h interval and increase further between the 0600–1200 h interval and the 1200–1800 h interval where the S_f concentrations reach their maximum value. The S_f concentrations decrease again through the evening, 1800–2400 h, into the early morning hours, 0000–0600 h. This diurnal pattern is not usually observed with flows from the SW or NW or during other seasons of the year except for late spring months (Fig. 2).

Local scale contributions to fine particle sulfur concentrations

The differences in the 24 h average concentrations, $\Delta[(S_f(U) - S_f(R)]$, average $+0.59\ \mu g\ m^{-3}$ when all of the first and fourth quarter measurements with E wind flows are used (Tables 2 and 3). The statistical significance of this value is high with $P \leq 0.0001$ by all tests used. As will be discussed in some detail later the formation of S_f by atmospheric oxidation of SO_2 should be minimal during the cooler months of the year in the St Louis area. Therefore it is reasonable to associate this value of $+0.59\ \mu g\ m^{-3}$ with the average contribution of primary local emissions of S_f within the St Louis area.

When there is NE wind flows the corresponding difference, $\Delta[(S_f(U) - S_f(R)]$, attributable to primary local emissions of S_f averages $1.2\ \mu g\ m^{-3}$ based on first and fourth quarter measurements. However the number of days with flows from the NE are low during these quarters of the year. A number of the air parcels associated with flow from the NE would have crossed the industrial areas immediately to the NE of the city of St Louis. The augmentation of the primary emissions of S_f by contributions from these industrial areas probably accounts for the higher value obtained.

The differences in the 24-h average concentrations, $\Delta[(S_f(U) - S_f(R)]$, average $+1.20\ \mu g\ m^{-3}$ when all third quarter measurements with E wind flows are used. This value is statistically significant by all tests but especially when matched days are used, $P = 0.0001$. If the average value of $+0.59\ \mu g\ m^{-3}$ obtained above and attributed to primary local emissions is subtracted, a residue value of $+0.61\ \mu g\ m^{-3}$ results. It appears reasonable to associate this value of $+0.61\ \mu g\ m^{-3}$ with S_f formed by atmospheric oxidation of SO_2 as air parcels are transported from the outer RAMS sites to those within the core urban areas of St Louis.

Table 3. Quarterly mean concentrations, standard error of means and number of daily values for fine particle S concentrations at non-urban in upwind air by wind flow direction into the St Louis area

Quarter	Year	Fine particle S concentration ($\mu g\ m^{-3}$) NE	SE	E	SW	NW	W
3rd*	1975	3.56,0.71,14†	3.81,0.54,21†	3.71,0.42‡	3.49,0.38,27	2.19,0.60,22	2.91,0.35
4th	1975	2.61,0.45,10†	2.01,0.16,31†	2.05,0.16‡	1.95,0.17,28	1.05,0.15,19	1.59,0.13
1st	1976	1.75,0.19,6†	1.85,0.18,24†	1.83,0.15‡	1.42,0.15,26	1.18,0.08,34	1.28,0.08
2nd	1976	2.52,0.49,14	2.95,0.38,21†	2.78,0.30	3.04,0.44,29	1.71,0.47,16	2.57,0.34
3rd*	1976	2.33,0.47,6	6.37,0.82,15†	5.21,0.72‡	3.23,0.35,26	2.39,0.43,13	2.95,0.28
4th	1976	1.71,0.19,5†	1.91,0.22,9†	1.84,0.16‡	1.49,0.13,28	0.90,0.11,29	1.19,0.09
1st	1977	ID	1.91,0.13,25†	1.90,0.13	1.46,0.20,22	1.37,0.13,37	1.40,0.11

* The larger mean particle S concentrations for each quadrant during the third quarter compared to the same quadrants during the first and fourth quadrants are statistically significant (Wilcoxon 2-sample test), $P \leq 0.1$, except for NE quadrants in 1976.

† These larger mean particle S concentrations with wind flows from the NE or SE compared to those from the NW are statistically significant (Wilcoxon 2-sample test), $P \leq 0.02$ (NE) or $P \leq 0.003$ (SE).

‡ These larger mean particle S concentrations with wind flows from the E compared to the W are statistically significant (Wilcoxon 2-sample test), $P \leq 0.06$.

Augmented concentrations of S_f have been observed to occur on individual days during episodic periods as air parcels are transported across the St Louis area (Altshuller, 1985). On such days high O_3 concentrations are also observed both in the air transported from upwind and in the air within and downwind of St Louis. These results are consistent with associating the residue value of 0.61 $\mu g\,m^{-3}$ during the third quarters with atmospheric oxidation of SO_2 to S_f on a local scale.

The % of the observed 24-h average S_f concentrations attributed to local scale processes by use of the expression $[S(U)-S(R)]$: $S(U)$ range from 5 % to 48 % depending on wind flow quadrant and the quarter of the year. The higher local scale contributions on a % basis occur when the flow is from the NE, 26–48 %, or NW, 18–30 %, rather than from the SE, 6–26 %, or from the SW, 15–26 %.

The results reported earlier in this work indicate that incremental $S_f(U)$ concentrations occur between the time periods $\Delta[(1200–1800)h-(0600–1200)h]$ during the warmer months of the year with flows from the E. The average increments are 0.87 $\mu g\,m^{-3}$ at site 103 and 1.00 $\mu g\,m^{-3}$ at site 105 from the measurements during the third quarters of 1975 and 1976. These differences in means are statistically significant for matched days at $P = 0.05$ at site 103 and $P = 0.01$ at site 105 for the tests applied. These incremental values are somewhat larger than the value of 0.61 $\mu g\,m^{-3}$ obtained above from the 24-h average difference in S_f between outer and urban sites.

The photochemical potential in the atmosphere is relatively small until the late morning hours because of the lower temperatures and much lower ultra-violet solar intensities earlier in the morning (Kelly *et al.*, 1984). The time period between 1000 and 1800 h is of especial interest. Any contributions to S_f at ground level which can be associated with SO_2 conversions within cumulus cloud droplets would also occur within this time period.

The monthly mean wind speeds during the months within the third quarters of 1975 and 1976 ranged from 7.6 to 10.8 $km\,h^{-1}$. The distances from the several outer sites to the urban sites range from 25 to 50 km. The longest transport time applicable is about 8 h during the time period with substantial photochemical potential. Therefore on a monthly average basis the maximum transport distance is ~ 86 km. The maximum transport distance would be slightly greater during spring months because of higher wind speeds. Consequently during a portion of a 1000–1800 h period air parcels will be upwind of the outer ring of RAMS monitoring sites. However the air parcel trajectories usually will be close enough to the St Louis area to consider that the processes involved are associated with the local rather than the regional scale. Therefore the incremental values of 0.87 $\mu g\,m^{-3}$ and 1.00 $\mu g\,m^{-3}$ obtained above can be attributed to atmospheric conversion of SO_2 to S_f on a local scale. These somewhat larger values than the 0.61 $\mu g\,m^{-3}$ obtained from the 24-h average differences in S_f concentrations above are consistent with the somewhat longer transport distances and conversion times involved in this latter procedure.

The decreases in S_f concentration during the evening and early morning hours observed at urban sites in St Louis are also likely to be associated with local scale processes. The lower wind speeds should result in the air parcels during these hours being within or near the St Louis area. Unlike O_3 which can undergo removal during the evening and morning hours by chemical conversion through reactions with NO or olefinic hydrocarbons (Altshuller, 1983; National Research Council, 1977; U.S. Environmental Protection Agency, 1978), chemical removal processes do not apply to fine particle S. Precipitation scavenging of S_f was infrequent during the third quarters of the year including the evening and night-time hours. Dry deposition may account for a portion of the decrease in S_f concentrations during these time periods.

Dry deposition fluxes usually are considered to be proportional to the concentration of the species of interest (Hicks, 1984). Therefore higher S_f fluxes should be associated with the much higher S_f concentrations measured during the warmer months of the year (Fig. 1, Tables 2 and 3). However the rates of removal by dry deposition of particle S are poorly established over most types of terrain (Hicks, 1984). The observed diurnal concentration patterns during the third quarters of the year would be consistent with a moderate rate of removal by dry deposition during the evening and night-time hours.

Early morning fog in the absence of precipitation occurred on about one third of the total days during the third quarters of 1975 and 1976. Another possible removal process for S_f during the night would be through scavenging into fog droplets. Once scavenged the particle S would not be detectable in the fine particle mode. Early in the morning as the fog dissipates during summer mornings the SO_4^{2-} could reappear as fine particle S and be measured as such. Additional S_f could be formed within the fog droplets if those oxidants are incorporated into the droplets which are capable of converting SO_2 to SO_4^{2-} during the night-time hours. The net result could be an apparent removal of S during the night followed by a significant increase in S_f during the morning.

Regional scale contributions to fine particle sulfur concentrations

By comparison with the percentages of the S_f concentrations estimated to be associated with local scale processes over half and usually two thirds or more of the S_f appears to be attributable to regional scale processes. The % of the S_f concentration values likely to be associated with regional scale processes appears especially high when the winds are from the SE and SW quadrants.

The average increments in the S_f concentration, $\Delta[(0600–1200)h-(0000–0600)h]$, are 0.47 $\mu g\,m^{-3}$ at

site 103 and 0.44 $\mu g\,m^{-3}$ at site 105 during the third quarters of 1975 and 1976 with easterly flows. These differences in means are statistically significant for matched days at $P \leq 0.1$. Increments in S_f concentration occur during this time period during other seasons as well excepting the coldest months of the year.

During the morning hours downward mixing of atmospheric species trapped aloft overnight above the nocturnal inversion layer can bring these species down to the surface. Increases in O_3 concentrations resulting from this process in the St Louis area have been discussed (Evans, 1979; Godowitch, 1979). Particle S and other aerosols have been observed aloft as a result of aircraft measurements over a number of areas in the United States (Blumenthal *et al.*, 1984; Tommerdahl *et al.*, 1981). Based on these aircraft measurements it has been concluded that secondary aerosols and O_3 are often carried over from day to day above the nocturnal inversion layer (Blumenthal *et al.*, 1984).

The results from modeling the transport, conversion and removal of SO_2 from urban and power plant plumes are consistent with these aircraft measurements (Gillani *et al.*, 1984). Multiday transport of S_f with continuing conversion of SO_2 to S_f is predicted to occur at least into the second day of transport.

These individual plumes during multiday transport can mix and reinforce each other resulting in layers which become isolated aloft as the nocturnal inversion develops during the evening. The next morning it appears reasonable that S_f along with other aerosol species and O_3 will be mixed down to the surface, thus contributing to the increase in S_f during the morning.

During the 0600–1200 h period it appears likely that several processes both regional and local in scale can contribute to the increase in S_f concentrations observed. An overlapping sequence of these processes may operate as follows: (1) early in the period the S_f increase may occur if night-time fog forms and dissipates with SO_4^{2-} scavenged into or formed in the droplets reappearing as S_f, (2) the S_f carried into the area from upwind in multiday transport being mixed down to the surface especially during the mid-morning hours, (3) a contribution to S_f near the end of this time period from local scale gas phase photochemical formation of S_f from SO_2.

The sum of all the contributions from various processes of either a local or regional scale discussed above appear to account for $\sim 2\,\mu g\,m^{-3}$ of the S_f concentration. During some quarters and with flows from some wind quadrants as much as an additional 3–4 $\mu g\,m^{-3}$ of S_f must be accounted for in the observed concentrations.

An examination of day to day variations in S_f concentrations during the warmer months of the year indicates that a substantial part of this additional 3–4 $\mu g\,m^{-3}$ is associated with the episodic periods discussed previously (Altshuller, 1985). A rapid accumulation of S_f occurs during such periods. Removal processes cannot keep up with this accumulation. These periods are associated with the slow passage of warm high pressure systems to the E of St Louis. Anticyclonic flows around these systems continue to bring increasing amounts of S_f into the St Louis area. It appears reasonable to associate the atmospheric photochemical formation and transport of S_f with the regional scale accumulation of precursor species, SO_2, volatile organic compounds and NO_x from high emission areas especially to the NE and SE of St Louis (Clark, 1980; Liu *et al.*, 1984; Gschwandtner *et al.*, 1986). The higher S_f concentrations in the flows from the SW compared to the NW also may be associated with these regional scale processes. However there also is the possibility during some periods that the S_f in flow from the SW is associated with transport from high emission areas in Texas (Clark, 1980; Gschwandtner *et al.*, 1986). Transport is augmented with the frequent presence of high velocity nocturnal jets during the spring and summer especially to the SW of the St Louis area (Evans, 1979).

The higher % of S_f concentrations associated with regional scale processes in flows from the SE and SW can be attributed to the higher potential for atmospheric conversions of SO_2 to S_f during long range transport from low latitudes.

The episodes of high S_f concentration can end with large decreases in S_f concentrations within a day or two. These situations occur with frontal passage of cleaner air masses from the W. Examples include an episode in early July 1975 associated with moderate precipitation and episode in mid July 1976 associated with only a trace of precipitation.

Chemical kinetic mechanisms in the conversion of SO_2 *to* SO_4^{2-}

The discussion above of the experimental results for S_f concentrations in the St Louis area and the interpretation of diurnal and seasonal patterns for these concentrations emphasizes the likely importance of photochemical processes in the oxidation of SO_2. Gas phase oxidation of SO_2 has been calculated to occur rapidly in summer with clear skies as a result of its reaction with hydroxyl radicals generated from the reactions of volatile organic compounds with NO_x in sunlight (Altshuller, 1979; Calvert *et al.*, 1978, 1985; Calvert and Stockwell, 1983) and possibly with Criegee intermediates (Calvert *et al.*, 1985; Calvert and Stockwell, 1983). It has been estimated that > 98 % of the SO_4^{2-} generated in gas phase reactions occurs as a result of reaction (1), likely followed by reactions (2) and (3)

$$HO + SO_2 (+ M) \rightarrow HOSO_2 (+ M) \quad (1)$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \quad (2)$$

$$SO_3 + H_2O \rightarrow H_2SO_4. \quad (3)$$

The rates of these reactions peak in mid-day in summer but the rates of conversions in summer have been calculated to convert one-third to one-half of the SO_2 present to SO_4^{2-} in a 24-h clear period (Calvert *et al.*, 1985).

Liquid phase processes within cloud and fog droplets can involve the oxidation of SO_2 by peroxides, especially by H_2O_2, by O_3 and possibly by HO and HO_2 radicals when transported within droplets (Calvert *et al.*, 1985; Chameides and Davis, 1982; Penkett *et al.*, 1979). All of these oxidizing species can be formed by gas phase reactions of volatile organic compounds with NO_x in sunlight. It is unclear to what extent H_2O_2 also may form within droplets.

Early morning fog droplets have been discussed briefly above as possible contributors to increasing concentrations of S_t during the morning. Experimental evidence for the formation of SO_4^{2-} within cumulus cloud droplets has been provided (Hegg *et al.*, 1984). In a modeling study the very rapid reactions of H_2O_2 with SO_2 as the source of appreciable conversion to SO_4^{2-} has been suggested as consistent with the lifetimes of cumulus clouds (Seigneur and Saxena, 1984). However it has not yet been demonstrated whether such reactions in cumulus clouds can lead to a significant contribution to ground-level concentrations of particle S during the afternoon.

There is direct experimental evidence for those situations in which elevated power plant plumes penetrate cumulus cloud layers for a 'burst' of oxidation of SO_2 caused by in-cloud processes (Gillani and Wilson, 1983; Gillani *et al.*, 1983). The frequency with which such events occur has not been determined.

The S_t concentrations decrease very substantially between the warmer and cooler months (Figs 1 and 2; Tables 2 and 3). Ratios as large as 10 can occur between the highest S_t monthly mean concentrations in the summer and the lowest monthly mean concentrations during the winter. Such results clearly indicate that the sum of all atmospheric processes, gas phase and liquid phase, must be much less effective during the winter.

At the latitude of St Louis the OH and HO_2 radical concentrations on a diurnal basis have been estimated to be 5–10 times lower during the winter than the summer (Altshuller, 1979). It follows that if such large decreases in OH radicals do occur the gas phase reactions should be far less important contributors to oxidation of SO_2 to SO_4^{2-} during the winter.

The formation of H_2O_2 involves reactions (1) and (2) below

$$HO_2 + HO_2 \xrightarrow{M} H_2O_2 + O_2 \quad (4)$$

$$2HO_2 + H_2O \rightarrow H_2O_2 + H_2O + O_2. \quad (5)$$

The rate expression for formation of H_2O_2 (Kircher and Sander, 1984) depends on the square of the HO_2 concentration, the water vapor content and the temperature. As indicated above the $[HO_2]^2$ radical concentration may decrease between summer and winter by factors of 25–100. A moderate decrease in rate constant with decrease in water vapor content in winter will tend to compensate for the increase in rate with decreasing temperature. Assuming H_2O_2 to be the rate-determining species, the rate of oxidation of SO_2 by H_2O_2 will decrease by as much as a factor of 100 from July to January at the latitude of St Louis.

The O_3 concentration in January in the inflow air into the St Louis area decreases by about a factor of three compared to July (Altshuller, 1986). Therefore, the reaction of O_3 with SO_2 within cloud droplets also should decrease substantially in winter compared to summer.

Possible influence from differences in values of meteorological parameters on the effects of wind direction on S_t concentrations

The substantial variations in meteorological parameters with season of the year can have significant effects on the rate of conversion of SO_2 to S_t as discussed in the previous section. There is the question whether within a season the differences in the values in meteorological variables between wind flow directions could explain the observed differences in the S_t concentrations. The effect of such variations in meteorological parameters has been investigated previously for O_3 concentrations (Altshuller, 1986; Shreffler and Evans, 1982). The procedure applied previously to O_3 (Altshuller, 1986) was also applied to S_t. As found for O_3 the S_t concentrations do tend to increase with increasing daytime temperatures and with decreasing daytime wind speeds. However a number of complexities with respect to the curves expressing the relationships make difficult the quantitative interpolation of the S_t concentrations to adjust for differences in meteorological parameters.

As a consequence a more useful approach was found to be the comparison of S_t concentrations with different wind flow directions when the values of the meteorological parameters were essentially the same. Those days whose values of temperature, solar radiation intensity and wind speed fell within the same relatively narrow ranges were selected with wind flows from the E and from the W. The comparisons were made for days when the S_t concentrations were in the upper part of the distribution curve during warmer months of the year. The results obtained for two ranges of meteorological parameters are given in Table 4. Despite the ranges of the meteorological parameters being almost identical the mean S_t concentrations with E flows are 1.5 times higher than with westerly flows. Also listed, the corresponding mean inflow O_3 concentrations are high for these groups of days indicating substantial photochemical potential for atmospheric oxidation of SO_2 to S_t.

These results indicate that the higher S_t concentrations with E flow occur even when there are no significant differences in the values of meteorological parameters with wind flow direction. Instead as discussed earlier these results are consistent with the cause of the higher S_t concentrations being the higher emissions of SO_2, VOC and NO_x associated with E wind flows.

Table 4. Fine particle S concentrations stratified by meteorological parameters

Intervals for meteorological parameters			Direction	Means of stations	103/105	Means inflow	Means inflow
T (°C)	WS (m s^{-1})	SR (lym^{-1})	of flows°	part. S concn 1200–1800 h	(μg m^{-3}) 24 h	part. S concn 24 h (μg m^{-3})	O_3 concn 1200–1500 h (μg m^{-3})
28.4–30.4	1.0–1.8	0.82–1.05	0.0–179.9	10.5	9.3	7.3	198
28.1–30.6	1.1–1.7	0.85–1.10	180.0–359.9	7.0	6.3	5.0	188
24.3–27.6	2.1–2.9	0.80–1.17	0.0–179.9	6.5	5.4	4.3	158
24.5–27.7	2.3–2.9	0.81–1.06	180.0–359.9	4.2	3.9	2.9	142

CONCLUSIONS

Slightly over three-quarters of the fine particle S, S_f, concentration measured near the center of the urban area at RAMS stations 103 and 105 are measured on average in air from upwind passing rural stations outside of St Louis. These results are consistent with a large regional/synoptic scale component contributing to the S_f concentrations measured within the urban area of St Louis and most likely other urban areas in midcontinent.

Local scale contributions to S_f concentrations are estimated on average to be as follows: (1) about 0.6 μg m^{-3} of S_f associated with primary local scale emissions of S_f, (2) from 0.6 to 1.0 μg m^{-3} of S_f associated with atmospheric conversions of SO_2 to S_f during local scale transport of SO_2 into the urban area of St Louis. However with wind flows from the NE quadrant the primary local scale emissions are estimated to somewhat exceed 1 μg m^{-3} of S_f. This higher contribution from local scale S_f emissions is attributed to flow across the industrial areas just to the NE of the City of St Louis. In addition a portion of the average increment in S_f Table 4 concentrations between early and late morning of $\sim$ 0.45 μg m^{-3} can be attributed to local scale processes. These processes are likely to involve (1) formation of S_f in fog droplets and subsequent dissipation of the droplets during the morning, (2) late morning atmospheric conversion of SO_2 to S_f. All of the local scale processes identified sum to account for $< 1/2$ of the observed S_f concentrations with the windflow from any of the wind quadrants. The local scale processes can account for $< 1/3$ of the observed S_f concentrations during several quarters of the year when the wind flows are from the SW and especially when the wind flows are from the SE.

Higher S_f concentrations usually are observed when the wind flows are from the E rather than from the W. This difference in S_f concentrations is associated primarily with the consistently lower S_f concentrations observed when the wind flows are from NW quadrant. The lower S_f concentrations with NW wind flows are consistent with previous observations (Altshuller, 1973; Decker *et al.*, 1976). Much lower SO_4^{2-} concentrations were measured at monitoring stations in the region to the NW of St Louis compared to SO_4^{2-} concentrations in the region to the NE. It is demonstrated especially during the warmer months that such differences in S_f concentrations between wind quadrants from the E and W cannot be explained by differences in the values of meteorological parameters such as temperature, solar radiation intensity or wind speed.

The higher S_f concentrations measured in E wind flows into St Louis appear to be best explained as associated with the greater accumulations of precursors and the subsequent regional scales atmospheric reactions of SO_2 in the presence of volatile organic compounds, NO_x and sunlight. The highest day to day concentrations of S_f concentrations during the warmer months are best related to such accumulations of precursors and atmospheric reactions during the slow passage of warm high pressure systems as they pass to the E of St Louis. Anticyclonic wind flows transport such reaction products as S_f and O_3 formed from the accumulated emissions into the St Louis area.

The higher S_f concentrations observed with wind flows from the SW compared to the NW also may be associated with anticyclonic flows bringing the reaction products from the higher emissions of precursors to the E around and into St Louis from the SW quadrant. In addition, there may be a contribution in SW flow from large emission sources in Texas. These emissions and their reaction products can be moved rapidly N in the high velocity nocturnal jets present in this region, especially during the spring and summer.

Much lower S_f concentrations are observed in the cooler compared to the warmer months. These lower concentrations of S_f are consistent with the much lower rates associated with both the gas phase and liquid phase atmospheric conversions of SO_2 to S_f during the cooler months.

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